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ON THE STRUCTURE OF CHEMISORBED ACETYLENE AND ETHYLENE ON NI, P--ETC(U)
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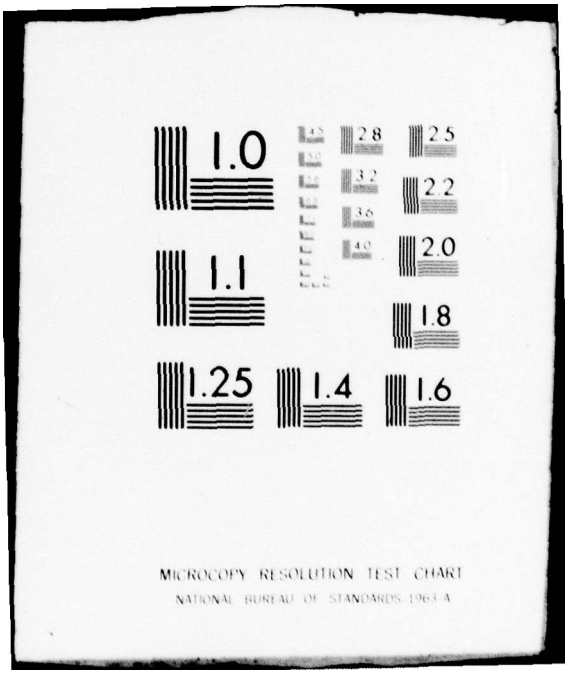
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On The Structure of Chemisorbed Acetylene and Ethylene on Ni, Pd and Pt Surfaces

by

J. E. Demuth

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The deduced geometries of chemisorbed ethylene are found to differ only slightly from those determined without considering these effects, but for acetylene two classes of structures are found. One class of structures is weakly distorted while the other is strongly distorted ($\sim sp^{2.5}$ hybridization). The latter structure is consistent with recent vibrational loss studies of chemisorbed ethylene on Ni shows relatively weak distortions. More subtle crystallographic and structural effects for acetylene and ethylene on (111), (100) and (110) Ni surfaces are also discussed.

On The Structure of Chemisorbed Acetylene and Ethylene on Ni, Pd and Pt Surfaces†

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Filtered He II ($h\nu$=40.8 eV) photoemission spectra for acetylene and ethylene molecularly chemisorbed at T ~ 100K on Ni(111), Ni(100), Ni(110), Pd(111) and Pt(111) have been obtained. The resulting vertical ionization potentials are presented and used within the framework of an approximate model to obtain information on the geometric structure of these molecules. Two initial state effects are discussed which are found to be important in deducing the molecular structures. These include an initial state shift of the lowest lying carbon-2s derived orbital and a metal atom induced shift of the σ_{CC} valence orbital for strongly distorted species. The magnitudes of both effects are estimated, the later using Hartree-Fock LCAO calculations of Be interacting with acetylene or ethylene.

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I. INTRODUCTION

A knowledge of the molecular geometry of chemisorbed hydrocarbon molecules on transition metal surfaces is necessary to fully understand chemisorption bonding and surface reactions of hydrocarbons. In previous papers we presented and discussed a method by which geometric information could be obtained from the observed photoionization levels of chemisorbed hydrocarbons [1,2]. Within the uncertainties of the forementioned analyses, it was found that the geometry or state of hybridization could be determined provided that enough valence ionization levels were experimentally visible [2]. This allowed the determination of the molecular geometries of ethylene on Cu, Ni, Pd and Pt(111) surfaces but prohibited an explicit geometry to be determined for chemisorbed acetylene. For the case of chemisorbed acetylene a low lying valence level was not completely separable from the background and introduced uncertainties into the analysis. Recently, these low-lying ionization levels have been measured using filtered $h\nu$=40.8 eV radiation [3] and have been found to lie at a lower energy than previously expected [2,3]. Also, Norman has recently shown that for "distorted" ethylene interacting with $Pt(PH_3)_2$, the Pt atom can affect the location of the high lying σ-orbitals [4].

In this paper we consider the consequences of both types of effects in our structural analysis of acetylene and ethylene on a variety of Ni, Pd and Pt surfaces. We show that a strongly distorted geometry for chemisorbed acetylene on Ni, Pd and Pt(111) surfaces is also consistent with the observed ionization levels. This alternate structure for chemisorbed acetylene is now consistent with the structures deduced on Ni(111) and Pt(111) by vibrational loss spectroscopy [5,6]. For ethylene chemisorbed on Ni(111), Pd(111) and Pt(111) we find that these effects do not strongly change the molecular geometries from those determined previously [2]. Also discussed are the differences in the structure of acetylene and ethylene on Ni(111), Ni(100) and Ni(110) surfaces as well as the possibility of counter rotations of the CH or CH_2 groups about the CC bond axis of chemisorbed acetylene or ethylene, respectively.

II. EXPERIMENTAL RESULTS

The entire valence orbital photoemission spectrum for acetylene and ethylene chemisorbed on a variety of surfaces at low temperatures (T ~ 100K) has been obtained using filtered $h\nu$=40.8 eV radiation as described elsewhere |3|. Low temperature adsorption is necessary to assure molecular adsorption and to preclude surface reactions which form new species |2,7|. In tables I and II we summarized the separations between the relative vertical ionization potentials of the σ-orbitals for acetylene and ethylene chemisorbed on Ni(111), Ni(100), Ni(110), Pd(111) and Pt(111) surfaces. The most significant feature of these new results is that for chemisorbed acetylene we can now clearly observe the lowest lying σ-orbital [3]. Previously, this level was not well resolved and occurred near the onset of $h\nu$=23.7 eV radiation so as to made it appear at smaller binding energies in the difference spectra |2,8|. For example, for acetylene on Ni(111) we find this level to be strongly broadened and lie at 16.7 eV below E_F instead of at 15.8 eV as suggested earlier |2,8|.

III. METHODOLOGY AND APPLICATION

The determination of the molecular structure from observed ionization levels is based upon a comparison of the relative changes in the ionization level spacings of the chemisorbed species from those observed for the free molecule and the relative energy level changes found in theoretical calculations. Here, one can in principle identify a molecular geometry which would produce the same changes in relative level spacings as calculated. In our case such calculations are highly simplified. Namely, we neglect final state effects and use calculations of distorted molecules which in some cases are bound to a metal atom. The rational for such an approach as well as the details of the methodology of such comparisons are discussed elsewhere |2|. We do note that recent theoretical work has also provided more insight as to one of the important sources of uncertainty in our analysis, i.e. the possibility of orbital-dependent changes in relaxation effects associated with the presence of the surface and metallic screening. Namely, calculations by Lang and Williams |9| suggest that such final

state effects are negligible since they find atomic – like screening for an atom bonded to the surface. We expect analogous molecular – like screening for a molecule on the surface.

A. Chemisorbed Acetylene

1. Acetylene on Ni(111)

To illustrate how we determine the structure by this method we shall discuss the geometry of acetylene on Ni(111). In Fig. 1 the hatched lines indicate the locus of possible CC bond distances and CCH bond angles calculated for a distorted free molecule which reproduces the experimentally observed relative change in level spacings of chemisorbed acetylene (to within ± .05 eV) from gaseous acetylene for the two highest lying σ-levels, the $2\sigma_u$ and $3\sigma_g$ levels. We will refer to this as the $2\sigma_u/3\sigma_g$ band. (The other shaded band will be discussed later.) From the changes in relative level spacings between the lowest lying-levels, the $2\sigma_g$ and $2\sigma_u$ levels, we generate three curves labeled 0, – ½ and – ¾. These curves correspond respectively to the locus of calculated geometries characteristic of the observed $2\sigma_g$ to $2\sigma_u$ level spacing and this observed spacing minus ½ and ¾ eV. (Here we consider the CH bond distance to vary with the state of hybridization of carbon, i.e., d_{CH} = 1.06Å to 1.10Å corresponds to d_{CC} = 1.21Å to 1.54Å).

Neglecting initial state effects (to be discussed), the intersection of the $2\sigma_g/2\sigma_u$ curve labelled "0" and the $2\sigma_u/3\sigma_g$ band correspond to a molecular geometry whose relative energy levels best match the observed changes in the relative level spacings of chemisorbed and free acetylene. This geometry falls into a range where we expect that we can reliably use free molecule calculations to obtain information about chemisorbed acetylene (called the "free molecule approximation"), |2|. The intersection of the $2\sigma_u/3\sigma_g$ band slightly above the $2\sigma_g/2\sigma_u$, –¾ eV curve (θ=168° and d_{CC}=1.23Å) corresponds to the 'preferred' geometry we had suggested previously |2|.

An added complication exists in determining the geometry of acetylene since the lowest lying σ-level, the $2\sigma_g$ level (and to a much lesser extent the $2\sigma_u$ level) appears to be shifted to larger binding energies due to an initial-state effect |3|. We can estimate the $2\sigma_g$ level shift for chemisorbed acetylene from our ethylene results since a geometry for chemisorbed ethylene can be determined based on all levels but the lowest lying $2\sigma_g$-level |2|. This procedure suggests a ½ eV shift of ethylene's $2\sigma_g$-level to larger binding energies. We expect a similar or slightly larger initial state shift for the $2\sigma_g$ level of chemisorbed acetylene. The consideration of this initial state shift in the $2\sigma_g$ to $2\sigma_u$ level separation leads to the curves labeled – ½ and – ¾ eV in Fig. 1. The intersection of these new curves with the $2\sigma_u/3\sigma_g$ band provides geometries for chemisorbed acetylene which are only slightly less distorted than the foremen-tioned geometries.

Another effect is also important for our spectroscopic analysis of the geometry of chemisorbed molecules. Namely, recent X–α SCF calculation by Norman |4| for distorted ethylene bonded to $Pt(PH_3)_2$ indicates a shift of a high-lying σ-level which was not observed in previous Xα SCF calculations for undistorted hydrocarbon molecules interacting with a transition metal atom |10,11|. (This shift differs from a screening effect of a lower σ-level which was noted |11| and whose effects on the structural determination have been discussed |2|). Using ab–initio SCF Hartree–Fock LCAO calculations (GAUSSIAN–70 |12|), we had previously examined the effects of a nearby metal atom, Be, on the geometric dependen-cies of the energy levels of the free acetylene molecule and found some extra shifts in a high-lying orbital for large geometric distortions. At that time we did not consider these in our analysis primarily since our determined geometries for acetylene appeared to lie well out of the range of distortions where these metal atom derived σ-orbital shifts occurred in our Be-C_2H_2 calculations. However, in view of Norman's results and recent vibrational loss studies |5,6|, we now consider in detail the implications of such metal atom induced level shifts in our geometry analysis.

In Fig. 2 we compare the geometry-derived changes in σ-level separations for the distorted acetylene molecule (denoted by +) and the distorted acetylene molecule interacting with a Be atom (denoted by o). Here the Be atom is located 1.95Å from each carbon atom so as to provide a reasonable carbon-metal bond length. Changes are shown for variations in either CC bond lengths or in CCH bond angles. These results show that the dependence of the relative σ-level spacings upon geometry is quantitatively similar for both free acetylene and acetylene bonded to Be except for one type of distortion. Namely, quantitative differences occur in the relative $3\sigma_g$ to $2\sigma_u$ level spacings for distortions having CCH angles greater than 150°. Here the $3\sigma_g$ level shifts closer to the $2\sigma_u$ level for C_2H_2 – Be than would occur for the same distortions in the free molecule. This metal atom induced shift in the $3\sigma_g$ level will alter the geometry deduced for chemisorbed acetylene. (We note that the magnitude of the $3\sigma_g$ shift is slightly dependent upon the location of the Be atom from the acetylene molecule.)

Accounting for the forementioned shift of the $3\sigma_g$-level for distorted acetylene, we estimate how this would affect the determined chemisorption geometry. Using the results of Fig. 2, we can determine a new locus of geometric structures. These are shown in Fig. 1 by the shaded $2\sigma_u/3\sigma_g$ band which diverges from the hatched band for CCH angles greater than 150°. The resulting intersection of this new 'set' of geometries with the geometries for the – ½ to – ¾ eV $2\sigma_g/2\sigma_u$ curves now indicates two possible geometries. The first geometry is still nearly identical to that found by considering only the free acetylene molecule. The second arises when we consider the Be-acetylene complex and the Be atom-induced shift of the $3\sigma_g$ level. This second structure has a CCH bond angle between 120° to 130° and a CC bond distance between 1.38 to 1.44Å. This second geometry corresponds roughly to a species having a state of hybridization between sp^2 and sp^3, roughly $sp^{2.5}$. This new geometry clearly lies out of the regime where we expect the "free molecule approximation" to be valid.

We might anticipate a similar $3\sigma_g$-orbital shift for acetylene interacting with Ni as with Be due to the similar s–character of the Ni wave function |13,17|. Thus, we postulate that the

observed ionization levels for chemisorbed acetylene on Ni can also be consistent with the second, strongly distorted geometry. (Clearly, a precise geometry for this more strongly distorted species can not be deduced from our present analysis.) Such a strongly distorted acetylene species is consistent with the acetylene geometry on Ni determined by Anderson |14|, the geometry characteristic of alkynes bonded to multi-Ni-atom organometallic compounds |15-16| and with recent vibrational loss measurements of acetylene chemisorbed on Ni(111) [6]. On the other hand, a strongly distorted geometry differs from that determined theoretically for acetylene bonded to a Ni atom by Upton and Goddard using ab-initio calculations |17|, as well as for acetylene, on a Ni cluster by Kobayashi et al. using CNDO calculations. Both of these latter theoretical studies show a weakly distorted structure for chemisorbed acetylene. In view of the vibrational loss results and the known structure of alkynes bonded to multi-Ni-atom organometallic compounds, we prefer to believe that acetylene is strongly distorted on Ni(111).

2. Crystallographic Effects in Bonding to Ni

If we use the same assumptions and consider our filtered $h\nu$=40.8 eV photoemission results for acetylene chemisorbed on Ni(110) and Ni(100) at T ~ 100K, we determine two possible structures on Ni(100) as found on Ni(111), but only one structure on Ni(110). For acetylene on Ni(100), the larger $2\sigma_g$-$2\sigma_u$ separation (after correcting for the same initial state shift as before) corresponds roughly to the – ½ $2\sigma_g/2\sigma_u$ curve in Fig. 1 while the $2\sigma_u/3\sigma_g$ band is displaced (~ 0.02Å) to slightly larger CC bond lengths. This results in two structures – the most strongly distorted having a CC bond length of 1.30-1.36Å and a CCH bond angle of 130-140°. In view of the previous discussion we believe that the strongly distorted structure is most likely.

For acetylene on Ni(110) the $2\sigma_g/2\sigma_u$ curve is pushed above the – ¼ $2\sigma_g/2\sigma_u$ curve of Fig. 1 while the $2\sigma_u/3\sigma_g$ band is now shifted to still larger CC bond lengths and has a more vertical contour. This results in only one geometry for acetylene on Ni(110) which has a CC

bond length of 1.27-1.32Å and a CCH bond angle of 145-150°. The occurrence of only one markedly distorted geometry on Ni(110) lends further support to the strongly distorted geometries on the other surfaces. In considering the strongly distorted geometries on all surfaces, we obtain a trend in these geometries in which the largest distortions occurs on Ni(111) and the weakest on Ni(110). However, the limitations of our present analysis require such trends be considered with caution. For example, both the carbon 2s initial-state shift and the $3\sigma_g$ shifts discussed for Ni(111) are likely to have some degree of substrate dependence which we cannot quantitatively predict.

2. Acetylene on Pd(111) and Pt(111)

The consideration of a similar $3\sigma_g$ orbital shift for chemisorbed acetylene on Pd(111) and Pt(111) also gives rise to two chemisorption geometries on these surfaces. We again prefer the strongly distorted geometry for acetylene on Pt(111) which is consistent with the geometry proposed on the basis of vibrational loss studies [5]. In Fig. 1 the corresponding locus of geometries for the $2\sigma_u$ to $3\sigma_g$ level separation for acetylene on Pt or Pd shifts the $2\sigma_g/3\sigma_g$ band to larger bond distances by ~ 0.02Å while the locus of geometries for the $2\sigma_g$ to $2\sigma_u$ level separation would lie between the 0 and $-\frac{1}{2}$ $2\sigma_g/2\sigma_u$ curve. From the general features of these curves, and considering a similar or greater $3\sigma_g$-orbital shift, we find the more strongly distorted geometry for acetylene on Pt or Pd to be slightly less distorted than that on Ni! Again however, such details should be considered with caution due to the likely differences in both the $3\sigma_g$-shift and the carbon 2s initial-state shift on Pt or Pd verses that on Ni (or Be). The preferred structures that we estimate for chemisorbed acetylene are summarized in Table III.

B. Chemisorbed Ethylene

1. Ethylene on Ni(111), Pd(111) and Pt(111)

For chemisorbed ethylene, we do not need to consider the initial state shift of the low lying carbon 2ss level, since there are enough higher lying σ-levels to uniquely determine the geometry. However as found for acetylene, a metal atom induced shift of one of the higher-lying σ-levels must must also be considered. Although this shift is comparable in magnitude to that found for acetylene, it does not give rise to a strongly different structure as found for acetylene. Instead, the number of σ-orbitals observed for ethylene as well as the particular orbital affected and the nature of the shift, give rise to only a small modification in our previously reported structures |2|. As found for acetylene, we find that undistorted ethylene bonded to either one Be atom or μ-bonded to four Be atoms does not show metal atom-induced changes in the relative (high lying) σ-orbital locations. This is shown in Fig. 3, for ethylene μ-bonded to a Be_4 cluster. Interestingly, this figure also shows that both the π-orbital and the 2ss orbital of ethylene bonded to Be are shifted relative to those of the free molecule as observed experimentally |1-3|. The resulting π-orbital shift also cautions interpreting experimentally observed π-orbital shifts on transition metals as arising from only π-d bonding!

If we now consider the case of a distorted ethylene molecule interacting with Be, we find that the σ_{CC} orbital (the $1b_{2g}$ orbital in Ref. |2|) shifts to a smaller energy - a similar effect as found for acetylene. In Fig. 4 we show how the σ_{CC} orbital of an "sp^3" distorted ethylene molecule shifts as a Be atom approaches the molecule, equidistant from both carbon atoms with the hydrogen atom bent directly away from the Be atom. The occurrence of this shift would produce level spacings for ethylene characteristic of a smaller HCH angle (see Fig. 8, Ref. 2) and slightly larger CC bond distances. Such a shift in the σ_{CC} orbital for ethylene on Pt or Pd would account for the unusually small HCH angles determined previously [2]. If we correct for a σ_{CC} orbital shift found for sp^3 rehybridized ethylene bonded to Be (using a C-Be bond distance of 1.97Å), we would determine a new HCH angle of ~ 110° instead of ~ 107°

found earlier |2| and a CC bond distance ~ .03Å larger. Such a geometry for ethylene on Pt(111) is consistent with recent vibrational loss studies |5|.

Similar considerations for ethylene chemisorbed on Ni(111) lead to a geometry with a negligibly smaller HCH bond angle than found earlier |2|. Hence, our earlier geometry for ethylene on Ni(111) is essentially unchanged [2]. This result is in agreement with ab-initio calculations of ethylene bonded to one Ni atom |17| as well CNDO calculations of ethylene bonded to a cluster of Ni atoms |18|. Such small distortions are also consistent with the close experimental similarities between the photoemission spectra of ethylene on Ni and Cu |2|, where on the latter substrate one certainly expects a weakly adsorbed "π-bonded" species. Unfortunately, vibrational loss measurements of ethylene on Ni(111) |6| have not yet been completely interpreted so as to enable a comparison. The estimated structures for chemisorbed ethylene on all surfaces studied are summarized in Table IV. We note that although the CC bond length and HCH bond angles are comparable, on all Ni surfaces, the HCC bond angle is noticeably smaller on Ni(100). This trend, although small, may be more meaningful than trends found for acetylene on Ni since neither the σ_{CC} shift nor the carbon 2ss level shift appear to be significant effects in our structural analysis of chemisorbed ethylene on Ni.

2. Axial Counter-rotations of the CH_2 groups

Another interesting question regarding chemisorbed ethylene is whether a counter rotation of the CH_2 groups about the C-C bond axis (total angle of ϕ) occurs upon chemisorption bonding. Such an effect might be expected to occur due to the partial occupation of molecular states of π^* symmetry associated with π-d bonding [19]. If so, it could account for the breakdown in symmetry observed in angle resolved, polarization dependent UPS studies |20|. The effects of such a rotation on the energy levels for planar ethylene are shown in Fig. 5. We also find that the relative shift of the σ_{CH}^* level shown in Fig. 5 is largely the same in the presence of a Be atom or for sp^3 hybridized ethylene. This behavior is also unique to this type

of distortion and cannot be created by combinations of other geometric distortions. We have the best chance to isolate such a shift in our analysis for weakly distorted ethylene where we need not consider the σ_{CC} shift described earlier. Although we find consistent displacements in the σ_{CH}^{*} peak positions for ethylene on all Ni surfaces, these shifts are within the uncertainties of our experimental measurements. This places an upper limit of 10° on the amount of rotation on Ni. For ethylene on Pd and Pt the metal atom induced σ_{CC} shift occurring for distorted ethylene precludes our isolating any corresponding effect.

We have also examined similar axial rotations of the CH groups in distorted acetylene. Here, we find that the $3\sigma_g$ - (σ_{CC}) orbital shifts to larger binding energies relative to the other levels which shift uniformly downward. This relative shift of the $3\sigma_g$-level is small and would require a rotation of ϕ=30° to exceed our experimental limits of uncertainty of 0.05 eV. Further the level shifts for other acetylene distortions prohibit us from uniquely isolating such rotational derived level shifts.

IV. SUMMARY AND DISCUSSION

In summary, we have extended our measurements and analysis of the ionization levels of chemisorbed acetylene and ethylene to determine their molecular structure. We find that the consideration of σ_{CC} orbital shifts, which occur when a strongly distorted molecule bonds to a nearby metal atoms, gives rise to an additional possible strongly distorted molecular geometry of chemisorbed acetylene on Ni, Pd and Pt (111) surfaces, but does not strongly change the geometries previously predicted for ethylene on these surfaces [2]. Physically, these σ_{CC} orbital shifts found for both distorted acetylene and ethylene appear to be the result of the exposure of the σ_{CC} charge density to the nearby metal atom. For the distorted molecule, the shielding and environment of the σ_{CC} electrons is changed - a situation to which we can attribute the observed breakdown of the distorted free molecule approximation used earlier [2]. Clearly, such effects for strongly distorted molecules complicate using observed ionization levels and free molecule calculations to obtain geometric information.

Although we cannot accurately calculate these shifts for transition metal atoms or surface atoms, we estimate them from our calculations with Be atoms. We also estimate the carbon 2s initial state shift for acetylene from our results for ethylene. Considering both effects, our analysis suggests that two structures of acetylene may occur which have energy levels consistent with those observed. One structure is weakly distorted while the other is strongly distorted and corresponds roughly to a $sp^{2.5}$ hybridized species. The strongly distorted acetylene structure is consistent with the structure of organometallic alkyne compounds [15-16] and with recent vibrational loss studies of chemisorbed actylene on Ni and Pt [5,6], but inconsistent with ab-initio calculations which show a weakly distorted structure [17]. Consideration of the σ_{CC} shifts for chemisorbed ethylene show only small deviations from our previously determined molecular structures, ie. chemisorbed ethylene is weakly distorted on Ni but strongly distorted on Pd and Pt.

We have also estimated the relative structures of acetylene and ethylene on the different substrates and crystal faces studied. Since both the carbon 2ss shift and the σ_{CC} metal-atom induced shift are likely substrate and bonding site dependent, these estimated structures are highly tentative. We observe rather strong crystallographic effects for acetylene and weaker effects for ethylene on Ni - the latter being less subject to the forementioned uncertainties.

The possibility of counter rotations of the CH_2 and CH groups about the C-C bond axis of ethylene or acetylene have also been considered in our analysis. We can place an upper bound of 10° for such rotations in chemisorbed ethylene on nickel but cannot for the other systems studied. We note that negligible axial counter rotations (<1°) occur to the CH_2 groups of ethylene in Zeise's salt [21] where the other distortions are similar to those we find for ethylene on Ni. Also, our calculations of Be-C_2H_2 and Be-C_2H_4 show that such distortions are not favored energetically despite the occurrence of π^*-p bonding [22]. In retrospect, the breakdown in molecular symmetry observed in the forementioned UPS study of ethylene on Ni(100) does not need to arise from this particular rotation. It could alternately arise from

other axial asymetries of the molecular on the surface, such as for example, the inclination of the molecular plane of ethylene to the surface so as to facilitate a hydrogen bonding interaction [7,23].

The relatively weak distortions of ethylene on Ni are another interesting aspect of our analysis. We speculate that these weak distortions may be the result of additional interactions of ethylenes' hydrogen atoms with the surface [23] which may help stabilize the undistorted geometry, or from a difference in the nature of bonding or in the bonding sites of ethylene on Ni from that of acetylene. The possibility also exists that the weakly distorted molecular geometry for ethylene on Ni(111) may be related to the presence of an occupied surface state on clean Ni(111) [24] but which is unoccupied on Pd [25] (and likely Pt as well).

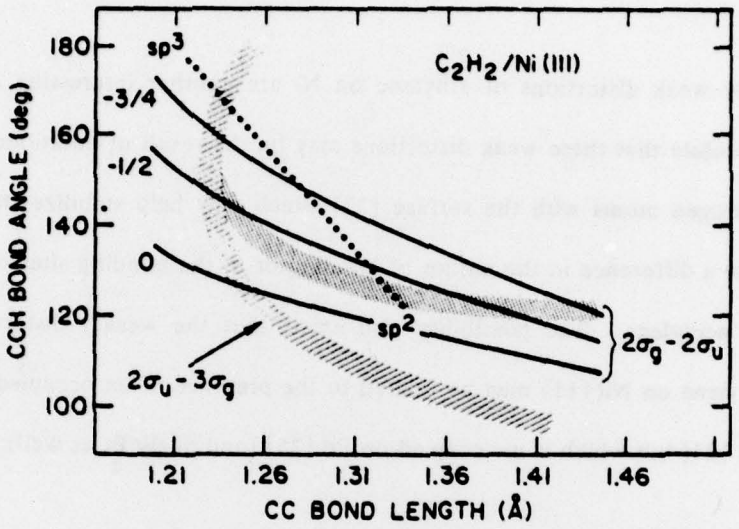

Figure 1. Structural parameters which describe the calculated and observed ionization level separations between the $2\sigma_u$ and $3\sigma_g$ levels (shown as hatched and shaded bands) and the $2\sigma_g$ and $2\sigma_u$ levels (shown as lines) for chemisorbed acetylene on Ni(111). The $2\sigma_g/2\sigma_u$ curves marked –½ and –¾ show the effects of inclusion of a ½ eV or ¾ eV initial state shift in the $2\sigma_g$ level. The shaded $2\sigma_u/3\sigma_g$ curve shows the effect of including a metal atom (Be) induced shift of the $3\sigma_g$ level. The dotted line shows the geometric parameters expected for a chemisorbed molecule varying from sp to sp^2 to sp^3 hybridization.

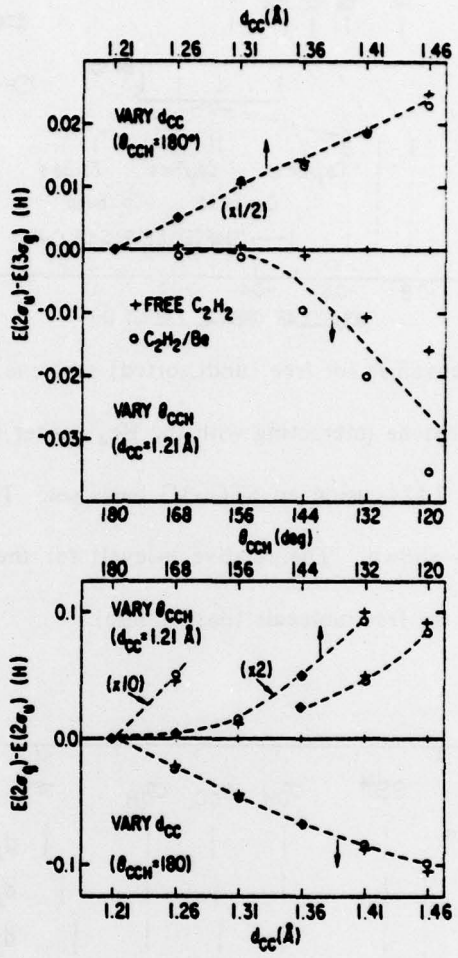

Figure 2. Calculated changes in relative orbital eigenvalues for free acetylene (+) and acetylene bonded to a Be atom (∘) as a function of molecular geometry (holding either d_{CC} or θ_{CCH} fixed). Here, $d_{C\text{-}Be}$ = 1.95Å. These calculations were done using an ab-initio SCF Hartree–Fock LCAO method (GAUSSIAN-70 |12|) with an STO-3G basis set.

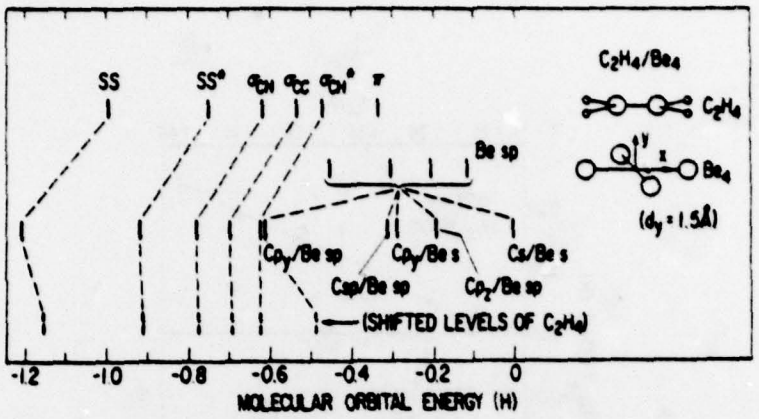

Figure 3. Molecular orbital eigenvalues for free (undistorted) ethylene, a Be_4 cluster, and the resulting levels for ethylene interacting with the Be_4 cluster (d_y = 1.5Å) calculated with GAUSSIAN–70 |12| using an STO–3G basis set. The orbital character of the admixed levels is shown. The relative σ-levels for the bonded molecule are compared to those of the free molecule (dashed line).

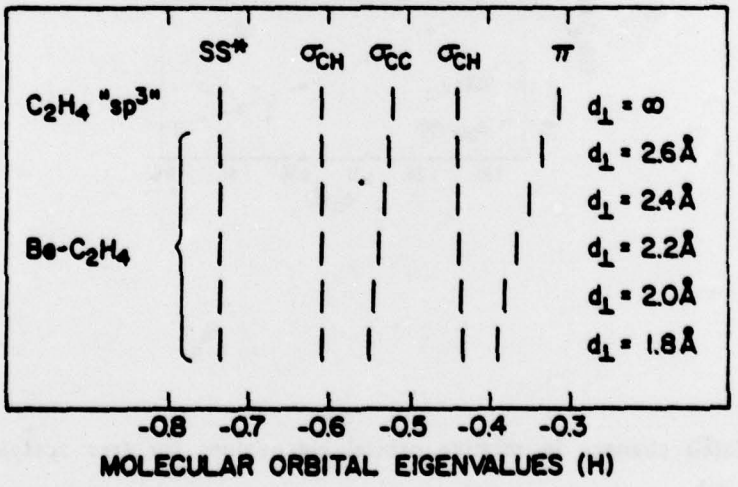

Figure 4. Molecular orbital eigenvalues for an isolated sp^3 hybridized ethylene molecule (top) and those (below) for the same molecule interacting with a Be atom calculated using GAUSSIAN–70 |12| with a STO–3G basis set. The distance between the Be atom and the midpoint of the CC double bond is indicated as $d_\perp$ where $d_\perp$ of 1.8Å corresponds to a C–Be bond distance of 1.92Å. Only the ethylene-derived orbitals are shown.

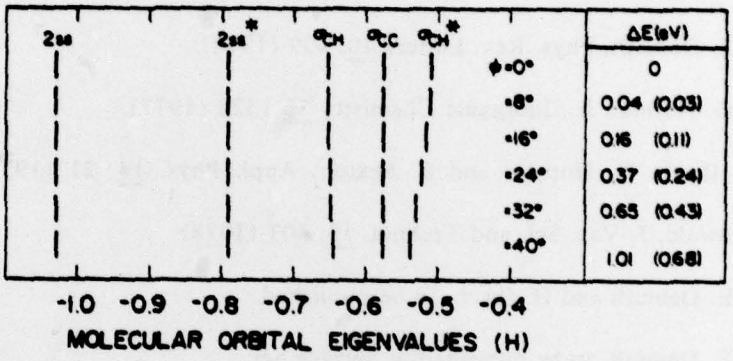

Figure 5. Molecular eigenvalues calculated using GAUSSIAN-70 [12] with a 4-31G basis set for planar undistorted ethylene (ϕ=o) and ethylene distorted via axial counter rotations ϕ of the CH_2 groups about the CC bond. The change in calculated Hartree–Fock energy is shown for distortions of the planar molecule and in parenthesis for distorted ethylene in an sp^3 configuration.

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Table I: Observed relative level separations in eV for gaseous, condensed and chemisorbed acetylene. The absolute location of the $3\sigma_g$ level in eV relative to the Fermi level is indicated where relevant. The level separations for gaseous acetylene are taken from refr. 3 and 26.

	$2\sigma_g/2\sigma_u$	$2\sigma_u/3\sigma_g$	$3\sigma_g$
gaseous C_2H_2	4.5	2.1	–
condensed C_2H_2	4.6	2.1	–
C_2H_2 on Ni(111)	5.5	2.2	9.1
C_2H_2 on Ni(100)	5.8	2.3	8.7
C_2H_2 on Ni(110)	5.2	2.5	8.7
C_2H_2 on Pd(111)	5.2	2.25	8.9
C_2H_2 on Pt(111)	5.2	2.3	9.2

Table II: Observed relative level separations in eV for gaseous and chemisorbed ethylene. The absolute location of the highest lying σ level (the σ_{CH}^{*} level) in eV relative to the Fermi level is indicated where relevant. The level separations for gaseous ethylene are taken from references 3 and 26.

	2ss/2ss*	2ss*/σ_{CH}	σ_{CH}/σ_{CC}	$\sigma_{CC}/\sigma_{CH}^{*}$	σ_{CH}^{*}
gaseous C_2H_4	4.2	3.2	1.2	2.0	–
C_2H_4 on Ni(111)	4.4	3.6	1.2	1.7	6.45
C_2H_4 on Ni(100)	4.5	3.35	1.45	1.6	6.5
C_2H_4 on Ni(110)	4.6	3.5	1.3	1.65	6.4
C_2H_4 on Pd(111)	4.3	3.6	1.4	1.8	6.3
C_2H_4 on Pt(111)	4.2	4.0	1.4	1.4	5.8

Table III: Estimated molecular geometries for chemisorbed acetylene as described in text. (Axial counter rotations of the CH groups about the C-C bond axis have not been considered.)

	d_{CC} (Å)	θ_{HCH} (°)
C_2H_2 on Ni(111)	1.38-1.43	120-130
C_2H_2 on Ni(100)	1.30-1.36	130-140
C_2H_2 on Ni(110)	1.27-1.32	145-150
C_2H_2 on Pd(111)	1.34-1.39	122-132
C_2H_2 on Pt(111)	1.34-1.39	122-132

Table IV: Estimated molecular geometries for chemisorbed ethylene as described in the text.

	d_{CC} (Å)	θ_{HCC} (°)	θ_{HCH} (°)
C_2H_4 on Ni(111)	1.39	120	117
C_2H_4 on Ni(100)	1.39	114	117
C_2H_4 on Ni(110)	1.39	120	117-120
C_2H_4 on Pd(111)	1.47	112	108
C_2H_4 on Pt(111)	1.52	110	108

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